Isotopic Effect on Electrochemical CO2 Reduction Activity and Selectivity in H2O- and D2O-based Electrolytes over Palladium

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Isotopic Effect on Electrochemical CO_2 Reduction Activity and Selectivity in H_2O- and D_2O-based Electrolytes over Palladium

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The isotopic effect on the electrochemical CO_2 reduction reaction (CO_2RR) is investigated in this study. A higher CO_2RR selectivity over its competing hydrogen evolution reaction was observed in D_2O-based electrolytes compared with the H_2O-based counterparts, which can be attributed to the lower [D^+] concentration than [H^+].

The increasing demand for effectively mitigating the growing atmospheric CO_2 level promotes electrochemical CO_2 reduction reaction (CO_2RR) in aqueous electrolytes as one of the viable options.[1-3] This is because CO_2RR, coupled with renewable energy resources, can produce value-added chemicals as a resource for downstream thermochemical reactions, thus potentially enabling the net reduction of CO_2.[3] Extensive studies have shown that the conversion and selectivity (*i.e.*, total current density and Faradaic efficiency, respectively) of catalysts can be controlled by alloy formation,[4-6] phase transition,[7, 8] additives,[9] surface functional groups,[10-13] and different salts[14, 15] in the electrolyte. However, rarely has the isotopic effect of the aqueous media been explored.

The current study investigates the effect of deuterium oxide (D_2O) on CO_2RR over carbon-supported Pd (Pd/C, See Fig. S1 for X-ray diffraction pattern in ESI) with four different 0.1M alkali-ion bicarbonate electrolytes (0.1M $AHCO_3$ or 0.1M $ADCO_3$, A=Na^+ or K^+, See ESI for the experimental details). Interestingly, Deuterium-based electrolytes exhibited markedly lowered D_2 evolution reaction (DER) activity compared with the H_2 evolution reaction (HER) activity in H_2O-based electrolytes, which is ascribed to lower deuteron concentration ([D^+]) than proton concentration ([H^+]) in the corresponding electrolytes. Different [D^+] and [H^+] concentrations originated from the different dissociation constant (pK) of D_2O and H_2O.[16] In contrast to the suppressed DER activity, CO_2RR activity was enhanced in D_2O-based electrolytes, implying that the isotopic effect can allow for different product distribution in the synthesis gas (*i.e.*, CO/D_2 and CO/H_2 ratios).

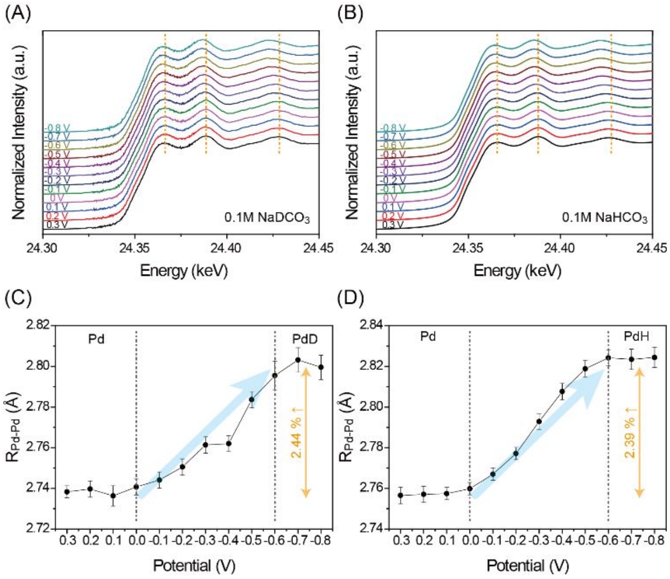

Fig. 1 *In-situ* XAFS analysis measured at Pd K-edge in different electrolytes. (A-B) *In-situ* XANES profiles from 0.3 V (bottom) to -0.8 V (top) in 0.1M (A) $NaDCO_3$ and (B) $NaHCO_3$ electrolytes. The dotted yellow lines are vertical lines to visualize the peak shifts. (C-D) *In-situ* EXAFS profiles in the same conditions.

It is well-known that H^+ is readily absorbed into Pd lattice to form Pd hydride (PdH) at potentials for CO_2RR.[6-8] This phase transformation thereby enables co-production of CO and H_2; otherwise, metallic Pd would be poisoned by CO, resulting in a negligible yield of CO production. In order to investigate if Pd forms Pd deuteride (PdD) like PdH formation, *in-situ* X-ray absorption fine structure (XAFS) analysis[17] was conducted (See ESI) from 0.3 V to -0.8 V versus reversible hydrogen electrode (RHE). Note that all of the potentials (V) in this study are versus RHE. With potentials being applied more negatively, X-ray

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Electronic Supplementary Information (ESI) available: X-ray diffraction pattern, EXAFS results, electrochemical data, TEM analyses. See DOI: 10.1039/x0xx00000x absorption near edge structure (XANES) spectra show the gradual shift toward lower energy, reflecting the progressive PdD and PdH formation under CO_2RR conditions in 0.1M $NaDCO_3$ and $NaHCO_3$ electrolytes, respectively (Fig. 1A-B). This result implies that the PdD formation likely occurs in the same manner as PdH formation, also evidenced by the interatomic distance profile of Pd and its first neighbor Pd (R_{Pd-Pd}) obtained from *in-situ* extended XAFS (EXAFS) analysis (Fig. 1C-D, Fig. S2 in ESI, and Supplementary Table S1). In each electrolyte, D^+(H^+) diffusion into Pd starts around 0 V and saturates around -0.6 V to form PdD(PdH) with an increase in R_{Pd-Pd} by ~2.4%, which is also consistent with the changes in the XANES peak positions.[7] Meanwhile, the coordination number of Pd remains similar, implying that the particle size is unchanged during CO_2RR (Fig. S3 in ESI).

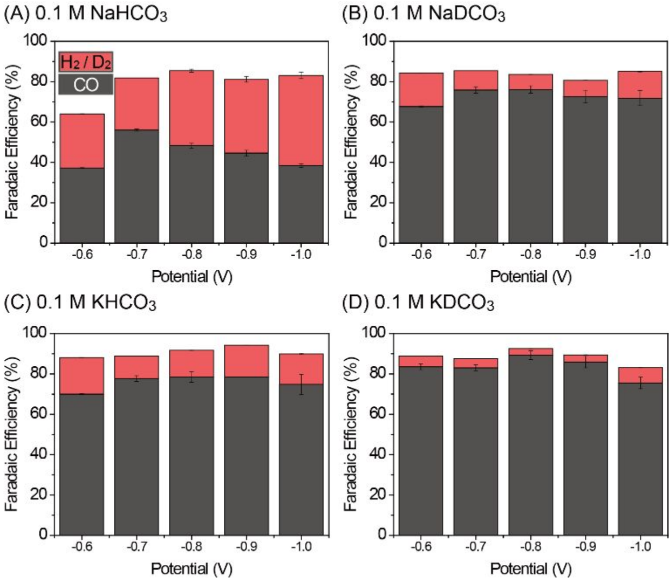

Fig. 2 Faradaic efficiency of CO and H_2 in different electrolytes. (A) 0.1M $NaHCO_3$, (B) 0.1M $NaDCO_3$, (C) 0.1M $KHCO_3$, and (D) 0.1M $KDCO_3$.

Fig. S4 in ESI shows the linear scanning voltammetry (LSV) curves of Pd/C in 0.1M $NaHCO_3$ and $NaDCO_3$ electrolytes saturated with CO_2 or Ar. Under the CO_2-saturated condition (Fig. S4A), similar LSV profiles are observed in both electrolytes. In contrast, it can be seen that, under the Ar-saturated condition (Fig. S4B), the current density in 0.1M $NaHCO_3$ electrolyte is higher than that in 0.1M $NaDCO_3$ electrolyte, indicating that a simple replacement of H_2O with D_2O can significantly reduce the DER activity, as will be discussed later in the product analysis. To investigate the isotope effect of D_2O on CO_2RR behavior, the activity of Pd/C was evaluated by using chronoamperometry (CA) techniques from -0.6 to -1.0 V with a potential interval of 0.1 V in 0.1M $AHCO_3$ or $ADCO_3$ electrolytes as shown in Fig. S5A-D (ESI). The CA current densities in all of the electrolytes are stable. The gaseous products were analyzed by using gas chromatography, and Faradaic efficiency (FE) of each product was calculated (See ESI). As displayed in Fig. 2, CO and H_2 (or D_2) are the main products in H_2O-based (or D_2O-based) electrolytes, with the sum of FE(CO) and FE(H_2/D_2) being near or over 90%. The only exception is at -0.6 V in 0.1M $NaHCO_3$, which might be attributed to the formation of oxygenated product (*i.e.*, formate), although the product yield is too low (~10^{-5} M) even after a prolonged CO_2RR period to be detected in the ^{1}H-NMR analysis (see the ESI). In addition, the long-term stability tests up to 8 hr at -0.8 V in D_2O-based electrolytes suggest that D_2O is an effective media for electrochemical CO_2RR (Fig. S5E in ESI). After 8 hr electrolysis, the FE(CO) values decreased by ~7 and ~12 % in 0.1M $KDCO_3$ and $NaDCO_3$ electrolytes (Fig. S6 in ESI), respectively, which seems to originate from catalyst agglomeration. This is also supported by transmission electron microscopy images taken before and after the long-term electrolysis, which show the well-dispersed Pd particles over C with a small increase in size (Fig. S7 in ESI).

However, the resultant product distribution, CO/H_2 or CO/D_2, can be significantly affected by changing H_2O with D_2O over the entire potential range. For example, Pd/C in 0.1M $NaDCO_3$ shows a FE(CO) of 76.1% at 0.8 V, which is 1.58 times higher than that (48.2 %) at the same potential in 0.1M $NaHCO_3$ (Fig. 2A-B). As the pH values of all electrolytes are near ~6.8, one can exclude the possibility that the CO_2RR performance is influenced by the pH effect. Therefore, such an enhancement can be explained by the different [D^+] and [H^+] concentrations in those near neutral-pH electrolytes. When H_2O is replaced with D_2O, [D^+] is roughly 33% of [H^+], owing to the higher pK value (14.491) of D_2O than that (13.995) of H_2O.[16] This leads to impaired DER activity in comparison with HER activity. As a consequence, more catalytic sites would be available for CO_2RR rather than DER, in turn enhancing FE(CO) in 0.1M $NaDCO_3$ over 0.1M $NaHCO_3$. Such an isotopic effect of D_2O is also observed in K-based electrolytes (Fig. 2C-D). The enhancement in FE(CO) in 0.1M $KHCO_3$ is attributed to the different hydrolysis capability of Na and K ions (so-called, cation effect),[14, 15] which is now well-established. Based on the observed FE trend in Fig. 2, one can conclude that, regardless of the salt choice, D_2O plays a role in facilitating CO_2RR activity and decreasing DER activity, mainly due to the lower [D^+] concentration.

It has been proposed that CO production primarily takes place *via* a carboxylic intermediate (*HOCO) while HER occurs *via* a hydrogen intermediate (*H) as shown in Fig. S8 (ESI).[18, 19] DER is expected to undergo a similar intermediate (*D) as the HER. The proposed mechanisms imply that the protonation (deuteration) step is involved in both CO_2RR and HER (DER),[18] which in turn suggests that the total current density (J(total)) would be influenced by the solvent choice. As shown in Fig. 3A, in the case that the same cation salt is selected, H_2O-based electrolytes exhibit slightly higher J(total) values than those in D_2O-based electrolytes, confirming that D^+/H^+ are involved in CO_2RR as well as DER/HER. On the other hand, regardless of the isotopic effect, K-based electrolytes show higher J(total) values than those in Na-based electrolytes, which is attributed to the cation effect described above.

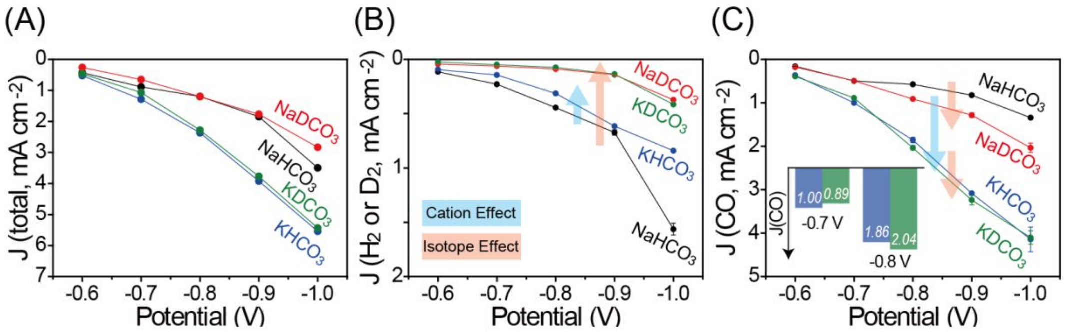

Fig. 3 Isotope and cation effects on CO_2RR. (A) Total current densities, (B-C) partial current density of (B) CO and (C) D_2 or H_2 with different electrolytes. Inset in (C) compares J(CO) values in 0.1M $KHCO_3$ (blue) and $KDCO_3$ (green) at -0.7 and -0.8V.

Fig. 3B shows the partial current density of D_2 and H_2 evolutions ($J(D_2)$ or $J(H_2)$) at different potentials. It is noteworthy that, upon replacing H_2O with D_2O, the DER activity is dramatically decreased compared to HER activity, which is consistent with the FE trend in Fig. 2. In contrast to the decreased DER activity, it is shown that both the cation and isotopic effects influence CO_2RR activity (Fig. 3C). In particular, the isotopic effect can be clearly observed in J(CO) profiles at -0.8 V and more negative potentials in Na-based electrolytes. This phenomenon can be understood in a way that DER is less likely to take place than HER, again due to the lower $[D^+]$ than $[H^+]$, promoting more catalytic active sites for CO_2RR and consequently enhancing J(CO). On the other hand, in K-based electrolytes, a relatively small enhancement of J(CO) is observed, indicating that the hydrolysis effect of the K ion is more influential on CO_2RR compared to the isotopic effect of D_2O.

It is interesting that J(CO) at low overpotentials in D_2O-based electrolytes is lower than or comparable to that in H_2O-based electrolytes in the same cation salt condition. For example, at -0.7 V, J(CO) value in 0.1M $KDCO_3$ is lower than that in 0.1M $KHCO_3$. However, with increasing overpotential more negatively, J(CO) values in 0.1M $KDCO_3$ get higher than those in 0.1M $KHCO_3$ (Inset in Fig. 3C). That is, at low overpotentials, higher $[H^+]$ is likely to facilitate higher CO yield in 0.1M $KHCO_3$ since the protonation step is also essential for CO_2RR. As the overpotential increases and J(CO) consequently increases, the CO yield is limited by the transport of CO_2. The J(CO) in 0.1M $KDCO_3$ surpasses that in 0.1M $KHCO_3$ in this case because DER, a main competing reaction, is less favorable than HER.

In summary, we demonstrate the isotope influence of D_2O on CO_2RR using a Pd catalyst. *In-situ* X-ray characterization confirms PdD formation, similar to the case of PdH formation in H_2O during CO_2RR. It is revealed that a simple replacement of H_2O with D_2O can not only decrease the DER rate due to the low D^+ concentration but also facilitate CO_2RR. Results from the current study provide a potentially useful methodology to tune the product distribution in other types CO_2RR reactions.

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Conflicts of interest

There are no conflicts to declare.

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The isotopic effect on the electrochemical CO_2 reduction reaction over palladium hydride and deuteride is explored in this study.